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U.S. PT

Attorney Docket No. 34061.830010.001

IN THE U.S. PATENT AND TRADEMARK OFFICE  
PATENT APPLICATION TRANSMITTAL

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Assistant Commissioner for Patents  
Washington, D.C. 20231

Dear Sir:

This is a request for filing a   X   Utility Patent Application under 37 CFR § 1.53(b). This application, entitled METHOD OF MANUFACTURING CITRIC ACID CHELATES, to Alan M ROBINETT & Carl SCHAUBLE,

is:            an Original, Nonprovisional  
  X   a Continuation  
           a Divisional  
           a Continuation-in-Part

Patent Application, with priority under 35 U.S.C. § 120 claimed from U.S. Patent Application Serial No. 08/755,236 filed November 22, 1996. Enclosed herewith is :

- An original specification, claims, drawing and Declaration and Power of Attorney:  
           pages of specification  
           pages of claims  
           pages of abstract  
           pages of drawings
- X   A true copy of the prior application, including the specification, claims, drawings, oath or declaration, and any amendments referred to in the oath or declaration as originally filed. Any such amendments referred to in the oath or declaration filed to complete the prior application did not introduce new matter therein.
- X   A Preliminary Amendment is enclosed to be entered in the new application after a filing date has been granted.
- X   A List of References.

The filing fee is calculated below:

	(Col. 1)	(Col. 2)
FOR:	NO. FILED	NO. EXTRA
BASIC FEE		
TOTAL CLAIMS	31 - 20 =	* 11
INDEP CLAIMS	4 - 3 =	* 1
<input type="checkbox"/> MULTIPLE DEPENDENT CLAIM PRESENTED		

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X   A check in the amount of \$ 1,114.00 is enclosed covering the \$1,086 filing fee and \$40 assignment recordation fee.

Please charge Deposit Account No. 08-2623 in the amount of \$\_\_\_\_\_.

Dated this 20th day of March, 1998.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Carol W. Burton", with a long horizontal flourish extending to the right.

Carol W. Burton, Reg. No. 35.465  
HOLLAND & HART LLP  
555-17th St., Suite 3200  
P.O. Box 8749  
Denver, Colorado 80201  
(303) 295-8357

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0827496 01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Alan M. ROBINETT & Carl SCHAUBLE

Serial No.

Filed: March 20, 1998

For: METHOD OF MANUFACTURING  
CITRIC ACID CHELATES

Examiner:

Art Unit: 1103

CERTIFICATE OF MAILING BY EXPRESS MAIL

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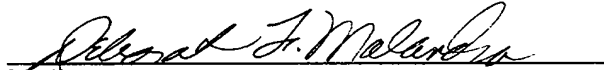
Sir:

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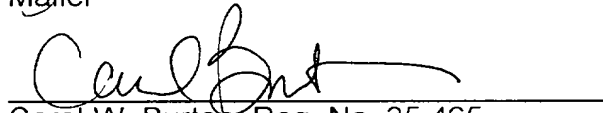
1. Patent Application Transmittal;
2. Copy of Specification, Claims, and Combined Declaration and Power of Attorney;
3. Check for \$1,114;
4. Preliminary Amendment;
5. Declaration Under 37 C.F.R. § 1.132 of Alan M. Robinett and Carl Schauble;
6. Information Disclosure Statement and Form 1449;
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this Certificate of Mailing by Express Mail relating to the above application, were deposited as "Express Mail", Mailing Label No. EM263016532US with the United States Postal Service, addressed to Assistant Commissioner for Patents, Box PATENT APPLICATION, Washington, D.C., 20231, on March 20, 1998.

March 20, 1998

  
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March 20, 1998

  
\_\_\_\_\_  
Carol W. Burton, Reg. No. 35,465  
HOLLAND & HART LLP  
555-17th Street, Suite 3200  
Post Office Box 8749  
Denver, Colorado 80201-8749  
Telephone: (303) 295-8357  
Facsimile: (303) 295-8261

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## 5 METHOD OF MANUFACTURING CITRIC ACID CHELATES

Field of the Invention

10 This invention relates to chelated metals having particular utility as plant micronutrients. More particularly, this invention relates to a method of manufacturing chelated metals for subsequent pre- or postemergent application to agricultural crops, either alone or in combination with other fertilizing material.

Background of the Invention

15 Micronutrients are those nutrients which are essential for plant growth but which are required in amounts which are typically less than that required for macronutrients such nitrogen, phosphorus and potassium. The seven micronutrients commonly understood to be necessary for plant growth are boron, chlorine, copper, iron, manganese, molybdenum and zinc. Cobalt, calcium, magnesium and sulfur may also be required in smaller amounts, and  
20 are variously classified as micronutrients or secondary nutrients. As used herein, the term micronutrients includes secondary nutrients.

The constituent elements of micronutrients must be presented to plants in a form suitable for plant uptake, translocation and assimilation. One way in which certain micronutrient metals have been successfully applied to and  
25 utilized by plants is by application of metal chelate solutions. The term chelate is from the Greek for claw, and describes a "complex" in which organic molecules form ring-like structures through coordinate bonds with metal ions. The metal chelate structure loosely ties up the constituent metal ion(s) in a form in which the metal component is less likely to dissociate or  
30 participate in chemical reactions when the chelate is in the soil or in solution with other fertilizers. This allows the chelated metal to remain available until after the product penetrates and translocates within plant.

Chelated metals are currently available in the fertilizer industry in powder and liquid forms. Each form has certain disadvantages, however, and

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both forms tend to be more expensive than inorganic metal compounds. For example, aqueous metal chelate formulations typically are supplied in 2.5 or five gallon plastic jugs containing from 5% to 9% by weight of the chelated metal. Cost of shipping these products is high, primarily because of the relatively low weight percent of the chelated metal in the product as compared to the volume of water in which the metal chelate is dissolved. In addition, if temperatures drop below 32°F some metal chelates crystallize out of liquid formulations and concentrate at the bottom of the container. Naturally this creates problems when subsequently applying the metal chelate solution to crops.

Not only does the bulkiness of the containers pose a storage space problem for some growers or fertilizer dealers, disposal of the plastic jugs can be problematical because many landfills no longer accept these containers because of container bulkiness and contamination issues. To address problems associated with use of plastic jugs, growers crops for which metal chelate requirements are substantial may choose to buy aqueous metal chelates solutions in bulk and place the liquids in large tanks or other storage vessels. However, to avoid accidental spillage when using such storage vessels, individual storage vessels are preferably placed in a lined dike having a capacity 110 % of the volume of the largest storage vessel. This technique involves substantial cost to the grower or fertilizer dealer, and does not obviate crystallization problems of metal chelate solutions at lower temperatures.

While powder metal chelates are available and solve some of the stability, storage and disposal problems associated with metal chelate solutions, other problems remain unaddressed. For example, to produce certain powdered metal chelates, constituents are reacted in an aqueous solution and then dried, a process requiring substantial time, energy and expense. Powdered metal chelates produced in this manner include ethylene diamine tetraacetic acid (EDTA) chelates and lignin sulfonate- based metal chelates. While these powdered metal chelates can provide the constituent metal in greater concentration than metal chelate solutions, (e.g., 6% to 15% weight percent), powdered metal chelates are substantially more expensive,

e.g., \$1.50 to \$8.00 per pound. The high cost of these products tends to limit their use to the horticulture industry.

Furthermore, some metal chelates solutions are decomposed by acid. The constituent metals may then exhibit reduced agronomic effectiveness.

5 Thus, mixing some metal chelate solutions, including reconstituted powdered metal chelates, with certain acidic fertilizers must be avoided prior to application of the metal chelate solution to plants. Yet application of micronutrients with macronutrient fertilizers is typically preferred, because it provides a way to more evenly distribute a small micronutrient volume over a  
10 large target acreage.

It is against this background that the significant improvements and advancements of the present invention have taken place.

#### Objects of the Invention

15 It is the principal object of the present invention to provide agricultural micronutrients in a form which is economical to transport and in containers with minimal disposal problems.

It is another object of the present invention to provide agricultural micronutrients in a form which may be combined with other fertilizer materials to create a stable composition in which the agronomic effectiveness of the  
20 micronutrients and the fertilizer material is maintained.

It is a further object of the present invention to manufacture agricultural micronutrients in a manner which does not require the removal of substantial amounts of water during processing and which has a shortened processing time over the processing time required to produce powdered EDTA metal  
25 chelates.

#### Summary of the Invention

In accordance with its major aspects, a method of manufacturing a composition specially adapted for subsequent solubilizing and application to agricultural crops is disclosed. The method of the present invention includes  
30 the steps of mixing a divalent metal salt, citric acid and sodium citrate to obtain a mixture having a moisture content most preferably of from approximately 10% to 1.25% by weight. The mixture is then processed in a drying environment to obtain a product which is partially chelated and which

has a moisture content less than that of the mixture prior to processing. The preferred drying environment has a temperature of from approximately 120°F to approximately 150°F. The mixture is preferably maintained in this drying environment for from approximately 50 seconds to approximately 70 seconds.

5 with the resulting product having a preferred moisture content of from approximately 5% to approximately 0.25% or less by weight of the final product, most preferably 1.25% to 0.5%. After processing in the drying environment, the product may be ground to reduce its average particle size. Thereafter, the ground product is placed in a container and hermetically  
10 sealed for shipment, and subsequent solubilization and use. The divalent metal of the divalent metal salt employed in the manufacturing method of the present invention is preferably selected from the group consisting of iron, copper, zinc and manganese.

A water soluble composition adapted for subsequent solubilizing and  
15 application to agricultural crops includes a partially chelated mixture of a divalent metal salt, citric acid and sodium citrate. The partially chelated mixture has a preferred moisture content of 1.25% or less by weight of the mixture. The divalent metal of the divalent metal salt employed in the manufacturing method of the present invention is preferably selected from the  
20 group consisting of iron, copper, zinc and manganese.

A more complete appreciation of the present invention and its scope can be obtained from the following detailed description of presently preferred embodiments of the invention, and the appended claims.

#### Detailed Description of the Invention

25 It has been discovered that by utilizing the method of manufacturing described below, a partially chelated citric acid product having a relatively low moisture content can be formed which may be stored for extended periods of time with minimal risk of degradation, further chelation or crystallization. The partially chelated citric acid products so produced are particularly suitable,  
30 after subsequent controlled hydration, for application as micronutrients to crops, either alone or in combination with other fertilizer material.

The preferred manufacturing method of the present invention initially involves the mixing of three primary reactants: (1) a divalent metal salt.

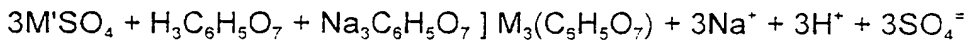
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(2) citric acid, and (3) sodium citrate, and the placement of this mixture in a drying environment. Prior to placement in the drying environment, the mixture preferably has a moisture content, by weight, of from approximately 10% to approximately 1.25%, with the most preferred moisture content, by weight of the total mixture, of from approximately 1.5% to approximately 1.25%. The primary reactants are preferably supplied to the mixture in molar ratios of 3:1:1 of divalent metal salt, citric acid, and sodium citrate, respectively. The preferred divalent metals are iron, copper, manganese and zinc. Suitable metal salts include sulfates, nitrates and phosphates.

The mixture is then heated in a controlled drying environment, producing a partially chelated product which has a total moisture content less than that of the mixture. The preferred moisture content of the partially chelated product, by weight, is from approximately 5% to 0.25%, with the most preferred moisture content of the final product, by weight, from approximately 1.25% to approximately 0.5%.

When a divalent metal sulfate is employed in the present invention, the equilibrium reaction established in the drying environment is:



Essentially, controlled dehydration and partial chelation of the mixture occurs in the drying environment, and a partially chelated citric acid product is produced thereby.

More particularly, Examples I-IV below describe the production of copper, zinc, iron and manganese citric acid products, respectively, which are partially chelated in accordance with the methods of the present invention. It should be noted that in addition to including the three primary reactants identified above, two secondary reactants are also added to the mixtures described in each example. Sodium tripolyphosphate is added as a wetting agent to the mixture in an amount equal to approximately 0.1% by weight of the final mixture. Monopotassium phosphate is added to condition the mixture, in an amount equal to approximately 2.5% by weight of the final mixture.

#### EXAMPLE I

1,600 pounds of copper sulfate salt (approximately 25% by weight

copper), 180 pounds of citric acid dry soluble 80% active ingredient (AI), 180 pounds of sodium citrate dry soluble 80% AI, 4 pounds of dry sodium tripolyphosphate, and 36 pounds of dry monopotassium phosphate (0-52-34) were mixed, with the total moisture content of the mixture preferably from approximately 1.5% to approximately 1.25% by weight of the mixture. The copper sulfate mixture was then placed on a continuous flow, fluidized bed drying operated in a temperature range of from approximately 120°F to approximately 150°F, which constituted a drying environment for the mixture. The mixture was maintained in the drying environment for from approximately 50 seconds to approximately 70 seconds, during which time the moisture content of the resulting product was reduced to approximately 0.5% by weight of the product, and the product was partially chelated. The resulting product, which included copper citric acid chelate, was dry and friable. The product was allowed to cool and stabilize, and thereafter was introduced into a high speed mill to reduce particle size of the product and to reduce the tendency of the product to agglomerate. The ground product was then placed in containers, for example, plastic packages of 8 mil or greater thickness, and hermetically sealed. The ambient environment in which the product was maintained after treatment in the fluidized bed and before hermetic sealing had a relative humidity of less than 50%.

#### EXAMPLE II

1,475 pounds of zinc sulfate salt (approximately 35% by weight zinc), 243 pounds of citric acid dry soluble 80% AI, 242 pounds of sodium citrate dry soluble 80% AI, 6 pounds of dry sodium tripolyphosphate, and 34 pounds of dry monopotassium phosphate were mixed, with the total moisture content of the mixture preferably from approximately 1.5% to approximately 1.25% by weight of the mixture. The zinc sulfate mixture was then placed on a continuous flow, fluidized bed drying operated in a temperature range of from approximately 120°F to approximately 150°F. The mixture was maintained in this environment for approximately 50 seconds to 70 seconds, during which time the moisture content was reduced to approximately 0.5% by weight, and part of the zinc sulfate salt was reacted to form zinc citric acid chelate. The product was allowed to cool, and stabilize, and thereafter milled. The ground

product was then placed in containers and hermetically sealed, as described above in Example I.

#### EXAMPLE III

1,350 pounds of iron sulfate salt (31% iron by weight), 200 pounds of  
5 citric acid dry soluble 80% AI, 200 pounds of sodium citrate dry soluble 80%  
AI, 6 pounds of dry sodium tripolyphosphate, and 244 pounds of dry  
monopotassium phosphate were mixed, with the total moisture content of the  
mixture preferably from approximately 1.5% to approximately 1.25% by  
weight of the mixture. The iron sulfate mixture was then placed on a  
10 continuous flow, fluidized bed drying operated in a temperature range of from  
approximately 120°F to approximately 150°F. The mixture was maintained in  
this environment for approximately 50 seconds to 70 seconds, during which  
time the moisture content was reduced to approximately 0.5% by weight, and  
part of the iron sulfate salt was reacted to form iron citric acid chelate. The  
15 product was allowed to cool, and stabilize, and thereafter milled. The ground  
product was then placed in containers and hermetically sealed, as described  
above in Example I.

#### EXAMPLE IV

1,350 pounds of manganese sulfate salt (approximately 31% by weight  
20 manganese), 200 pounds of citric acid dry soluble 80% AI, 200 pounds of  
sodium citrate dry soluble 80% AI, 6 pounds of dry sodium tripolyphosphate,  
and 244 pounds of dry monopotassium phosphate were mixed, with the total  
moisture content of the mixture preferably from approximately 1.5% to  
approximately 1.25% by weight of the mixture. The manganese sulfate  
25 mixture was then placed on a continuous flow, fluidized bed drying operated  
in a temperature range of from approximately 120°F to approximately 150°F.  
The mixture was maintained in this environment for approximately 50  
seconds to 70 seconds, during which time the moisture content was reduced  
to approximately 0.5% by weight, and part of the manganese sulfate salt was  
30 reacted to form manganese citric acid chelate. The product was allowed to  
cool, and stabilize, and thereafter milled. The ground product was then  
placed in containers and hermetically sealed, as described above in Example  
I.

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It has been discovered that the preferred products of the present invention are those manufactured in accordance with the procedures of Examples I-IV above, in which the mixture to be placed in the drying environment has a moisture content of 4% or less by weight. In contrast, when the finished product has a moisture content of 5% or more, the product tends to agglomerate after production and harden during storage. Product shelf life is reduced, and, in extreme cases, the hardened product cannot be solubilized and further chelation induced without regrinding the product. Also, the hardened product typically cannot be mixed with other fertilizer material without regrinding. Thus, it is preferred that the mixtures of the present invention have a total moisture content by weight not exceeding 4% and the final partially chelated product have a preferred moisture content by weight of from 0.25% to 3%, most preferably approximately 0.5%.

It has also been discovered that the preferred products of the present invention are those manufactured in accordance with the procedures of Examples I-IV above, in which the mixture to be placed in the drying environment having an ambient temperature of at least 101°F. Mixtures placed in a drying environment of 90°F to 100°F or less result in a partially chelated product which exhibits reduced solubility and reduced compatibility with some fertilizer materials. In addition, the product is susceptible to uncontrolled chemical reaction when the packaged product is stored in ambient temperature above 100°F, such as may be experienced in warehouses, truck trailers or other storage environments. Such uncontrolled chemical reactivity can result in destruction of product packaging and substantially reduced product shelf life. Thus, it is preferred that the mixtures of the present invention be treated in a drying environment of at least 101°F, preferably of from 101°F to 190°F, and most preferably from approximately 120°F to approximately 150°F.

It has also been determined that the manufacturing methods of the present invention have a limited degree of success when the mixtures described in Examples I-IV are maintained in a drying environment for at least 10 seconds and at most 30 minutes. It is preferred, however, that the mixtures be maintained in a drying environment for from 30 seconds to 5

minutes, with maintenance of the mixtures in a drying environment for approximately 50 seconds to approximately 70 seconds most preferred. Mixtures maintained in a drying environment for an excessive or insufficient period of time may have inconsistent moisture content and texture, and have a resultant reduction in shelf life, solubility and fertilizer compatibility.

Examples V-VIII below describe the solubilization and further chelation of the concentrated, partially chelated ground products manufactured above in accordance with Examples I-IV, respectively, to produce metal chelate solutions suitable for pre- or postemergent application to agricultural crops. In each of Examples V-VIII, the addition of water to the ground product results in the solubilization of the ground product and further chelation of the divalent metal of the particular divalent metal salt present in the ground product.

#### EXAMPLE V

Two and one half pounds of the partially chelated copper/citric acid product produced according to Example I were added to one gallon of water. The product was mixed until the resulting solution was clear.

#### EXAMPLE VI

Sixteen pounds of the partially chelated zinc/citric acid product produced according to Example II were added to 3 gallons of water. The product was mixed until the resulting solution was clear.

## EXAMPLE VII

Two and one half pounds of the partially chelated iron/citric acid product produced according to Example III were added to 1 gallon of water. The product was mixed until the resulting solution was clear.

## EXAMPLE VIII

Two and one half pounds of the partially chelated manganese/citric acid product produced according to Example IV were added to 1 gallon of water. The product was mixed until the resulting solution was clear.

To ascertain the solubility and stability in fertilizer solutions of the metal citric acid chelate solutions produced above in accordance with the preferred methods of the present, 25 grams of a partially chelated copper/citric acid mixture prepared in accordance with Example I was further chelated and dissolved in 83 grams of water to produce a copper/citric acid chelate solution (referred to in Table I as the "Chelate Solution"). Thereafter, 18 grams of each of 13 different fertilizer solutions was separately mixed with 1.7 grams of the Chelate Solution, and the resulting solution visually evaluated upon mixing and after two hours if any undesirable precipitation or crystallization occurred or other reaction products were produced. The evaluation results are summarized in Table I.

TABLE I

FERTILIZER SOLUTION	SOLUBILITY IN CHELATE SOLUTION INITIALLY UPON MIXING	SOLUBILITY IN CHELATE SOLUTION AFTER 2 HOURS
1. 25% urea solution (46-0-0)	Clear	Clear
2. 32% urea-ammonium nitrate solution	Clear	Clear
3. Potassium nitrate solution (13.8-0-46)	Clear	Clear
4. Ammonium polyphosphate (10-34-0)	Clear	Clear

5. Potassium chloride solution (0-0-62)	Clear	Clear
6. Potassium hydroxide (0-0-75)	Dark flocculant	Top 95% of solution clear, with flocculant settled at bottom of container
7. Calcium chloride solution (10% Ca)	Fine white precipitate	Top 95% of solution clear, with precipitate settled at bottom of container
8. Phosphoric acid solution (0-0-80)	Clear	Clear
9. Aqua ammonia solution (24-0-0)	Clear blue solution	Clear blue solution
10. 2.5% P <sub>2</sub> O <sub>5</sub> -1.5% K <sub>2</sub> O solution (0-15-0)	Insoluble at concentration	Insoluble at concentration
11. Ammonium thiosulfate (12-0-0 and 26 S)	Clear	Clear
12. 10% sodium lignosulfonate	Dark brown solution without precipitate or flocculant	Dark brown solution without precipitate or flocculant
13. Calcium nitrate (17-0-0 and 24 Ca)	Fine white precipitate	Top 95% of solution clear, with precipitate settled at bottom of container

By employing the methods of the present invention to manufacture a partially-chelated, citric acid product, complete solubilization and subsequent dehydration of the product during manufacture is not required. Substantial energy costs and the processing time associated with dehydration is

5 successfully avoided. Indeed, by not first solubilizing the primary reactants to

achieve chelation and then dehydrating the fully chelated product, large volumes of water are not required at the manufacturing site. In addition, because the partially chelated, citric acid products of the present invention do not contain substantial quantities of water, shipment costs associated with transport of micronutrient solutions are also avoided.

Moreover, the manufacturing methods and products of the present invention provide a micronutrient product which has a relatively high concentration of metal (approximately 20%-25% by weight), is economical to ship, requires less storage space than other metal chelates, and is easier to use in conjunction with other fertilizer materials. Storage problems associated with metal EDTA solutions, for example, crystallization, are minimized with the micronutrient products of the present invention. As described above, the partially chelated metal products produced in accordance with Examples I-IV described above do not appear to be susceptible to uncontrolled chelation, degradation or other reaction during storage at temperatures of up to 140°F for limited periods. Container disposal problems also associated with metal EDTA solutions are also avoided with the micronutrient products of the present invention. The preferred plastic bags used to package the products as described above in Examples I-IV. can be recycled or landfilled.

Presently preferred embodiments of the present invention and many of its improvements have been described with a degree of particularity. It should be understood that this description has been made by way of preferred examples, and that the invention is defined by the scope of the following claims.



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9. The method of claim 7 wherein the mixture has a total moisture content of from approximately 1.5% to 1.25% by weight of the mixture and the partially chelated product has a total moisture content by weight of from approximately 0.5% to approximately 1.25% of the product.

10. The method of claim 9 wherein the product has an average particle size and the method further comprises the steps of:

grinding the product to reduce the average particle size of the product;

5 placing the ground product in a container; and  
hermetically sealing the container.

11. The method of claim 10 wherein method further includes the step of:

maintaining the mixture in the drying environment for from approximately 50 seconds to approximately 70 seconds.

12. The method of claim 7 wherein the moisture content of the product is from approximately 1.25% to approximately 0.5% by weight of the product.

13. The method of claim 1 wherein the drying environment has a temperature of from approximately 120°F to approximately 150°F and wherein the mixture processing step includes the step of:

5 processing the mixture in a continuous flow, fluidized bed drying  
for from approximately 50 seconds to approximately 70 seconds.

14. The method of claim 1 further comprising the step of:

reacting the product with an aqueous solution to further chelate the product.

15. The method of claim 14 wherein the aqueous solution contains a fertilizer material which is not a chelated product.

16. A water soluble composition adapted for subsequent solubilizing and application to agricultural crops, comprising a partially chelated mixture of a divalent metal salt, citric acid and sodium citrate, wherein the partially chelated mixture has a moisture content of at most 1.25% by weight of the  
5 mixture.

17. The composition according to claim 16, wherein the divalent

metal of the divalent metal salt is selected from the group consisting of iron, copper, zinc and manganese.

18. The composition according to claim 16, wherein the partially chelated mixture has a moisture content of at most 0.5% by weight of the mixture.

19. The composition according to claim 18, wherein the divalent metal of the divalent metal salt is selected from the group consisting of iron, copper, zinc and manganese.

20. The partially chelated product produced in accordance with the process of claim 1, wherein the divalent metal is selected from the group consisting of iron, copper, zinc and manganese.

21. The partially chelated product of claim 20, wherein the partially chelated product has a moisture content of from 0.5% to 1.25%.

22. The partially chelated product of claim 20, wherein the mixture has a moisture content of from 1.25% to 5% by weight of the mixture.

## ABSTRACT

A method of manufacturing a water soluble composition adapted for subsequent solubilizing and application to agricultural crops is disclosed in which a divalent metal salt, citric acid and sodium citrate are mixed to form a mixture having a moisture content of from approximately 10% to 1.25% percent by weight. The mixture is then processed in a drying environment to produce a product which is partially chelated and has a moisture content which is less than the moisture content of the mixture prior to processing. The preferred drying environment is from 120°F to 150°F. Most preferably, the processing step is performed in a continuous flow, fluidized bed dryer at from approximately 120°F to 150°F for from approximately 50 seconds to approximately 70 seconds. Preferred divalent metals are iron, copper, zinc and manganese.

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COMBINED DECLARATION AND POWER OF ATTORNEY

DECLARATION:

As below named inventors, we hereby declare that:

Our residences, post office addresses and citizenship are stated below next to each of our names.

We believe we are the original and first joint inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled METHOD OF MANUFACTURING CITRIC CHELATES filed concurrently herewith.

The persons named as inventors in this application are Alan M. ROBINETT and Carl SCHAUBLE.

We hereby state that we have reviewed and understand the contents of the above identified specification, including claims.

We acknowledge the duty to disclose information which is material to the examination of this application in accordance with 37 C.F.R. § 1.56(a).

No prior applications or inventors' certificates have been filed.

POWER OF ATTORNEY:

As named inventors, we hereby appoint:

Carol W. Burton, Reg. No. 35,465;  
William J. Kubida, Reg. No. 29,664;  
Lee R. Osman, Reg. No. 38,260;  
Homer L. Knearl, Reg. No. 21,197;  
Earl C. Hancock, Reg. No. 19,472;  
F.A. "Sandy" Sirr, Reg. No. 17,265;  
Richard A. Bachand, Reg. No. 25,107;  
John R. Wahl, Reg. No. 33,044;  
Andrew D. Sorensen, Reg. No. 33,606; and  
John William W. Cochran, Reg. No. 26,652,

to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

Send all correspondence to:

Carol W. Burton, Esq.  
HOLLAND & HART <sup>LLP</sup>  
555 17th Street, Suite 3200  
P.O. Box 8749  
Denver, Colorado 80201-8749  
(303) 295-8357 (telephone)  
(303) 295-8261 (facsimile)

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We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Inventor's Full Name:	Alan M. ROBINETT
Inventor's Signature:	<i>Alan M. Robinett</i>
Date:	November 7, 1996
Residence: (City, State and/or country)	102 Twin Oaks Ozark, Alabama 36360
Citizenship:	UNITED STATES OF AMERICA
Post Address Office:	Same as above

Inventor's Full Name:	Carl SCHAUBLE
Inventor's Signature:	<i>Carl Schauble</i>
Date:	November 7, 1996
Residence: (City, State and/or country)	105 Country Club Drive Ozark, Alabama 36360
Citizenship:	UNITED STATES OF AMERICA
Post Address Office:	Same as above

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For: METHOD OF MANUFACTURING  
CITRIC ACID CHELATES

Examiner:

Art Unit: 1103

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

The present application claims priority under 35 U.S.C. § 120 of co-pending of U.S. Serial No. 08/755,236 filed November 22, 1996. A Petition for One-Month Extension was filed in Serial No. 08/755,236 on March 17, 1998, thereby maintaining co-pendency of Serial No. 08/755,236 while filing the present case.

Please enter the following amendments:

IN THE CLAIMS:

Please cancel claims 14, 15 and 19.

Please amend claims 1, 16 and 17 as follows:

1. (Amended) A method of manufacturing a water soluble composition adapted for subsequent solubilizing and application to agricultural crops, comprising the steps of:

5 mixing a divalent metal salt, citric acid and sodium citrate to obtain a nitrate-free mixture having a moisture content of from approximately 10% to 1.25% by weight; and

processing the nitrate-free mixture in a drying environment to obtain a nitrate-free product which is partially chelated and has a moisture content less than that of the mixture prior to processing.

16. (Amended) A water soluble composition adapted for subsequent solubilizing and application to agricultural crops, [comprising] consisting essentially of a partially chelated mixture of a [divalent] metal salt,

citric acid and sodium citrate, wherein the partially chelated mixture has a  
5 moisture content of at most 1.25% by weight of the mixture.

17. (Amended) The composition according to claim 16, wherein the  
[divalent] metal of the [divalent] metal salt is selected from the group  
consisting of iron, copper, zinc and manganese.

Please add the following newly-presented claims 23-34

23. A method of manufacturing a water soluble composition  
adapted for subsequent solubilizing and application to agricultural crops,  
comprising the steps of:

mixing a metal salt, citric acid and sodium citrate to obtain a  
5 nitrate-free mixture having a moisture content of from approximately 10% to  
1.25% by weight; and

processing the nitrate-free mixture in a drying environment to  
obtain a nitrate-free product which is partially chelated and has a moisture  
content less than that of the mixture prior to processing.

24. The method of claim 23 wherein the drying environment has a  
temperature of from approximately 120°F to approximately 150°F.

25. The method of claim 23 wherein the drying environment has a  
temperature of from approximately 120°F to approximately 150°F and  
wherein the mixture processing step includes the step of:

maintaining the mixture in the drying environment for from  
5 approximately 50 seconds to approximately 70 seconds.

26. The method of claim 23 wherein the moisture content of the  
product is approximately 5% to approximately 0.25% by weight of the product.

27. The method of claim 23 wherein the moisture content of the  
product is approximately 1.25% to approximately 0.5% by weight of the  
product.

28. The method of claim 23 wherein the product has an average  
particle size and the method further comprises the steps of:

grinding the product to reduce the average particle size of the  
product;



5 placing the ground product in a container; and  
hermetically sealing the container.

29. The method of claim 23 wherein the metal of the metal salt is selected from the group consisting of iron, copper, zinc and manganese.

30. The method of claim 29 wherein the mixture has a total moisture content of from approximately 1.5% to 1.25% by weight of the mixture and the partially chelated product has a total moisture content by weight of from approximately 0.5% to approximately 1.25% of the product.

31. A water soluble composition adapted for subsequent solubilizing and application to agricultural crops, comprising a nitrate-free, partially chelated mixture of a divalent metal salt, citric acid and sodium citrate, wherein the partially chelated mixture has a moisture content of at  
5 most 1.25% by weight of the mixture.

32. The composition according to claim 31, wherein the divalent metal of the divalent metal salt is selected from the group consisting of iron, copper, zinc and manganese.

33. The composition according to claim 31, wherein the partially chelated mixture has a moisture content of at most 0.5% by weight of the mixture.

34. The composition according to claim 33, wherein the divalent metal of the divalent metal salt is selected from the group consisting of iron, copper, zinc and manganese.

#### REMARKS

Claims 1-22 were presented in co-pending Serial No. 08/755,236, a copy of which is attached. In the above amendments, claims 14, 15 and 19 are canceled, claims 1, 16 and 17 are amended, and claims 23-34 are newly presented. Claims 1-13, 16-18 and 20-34 are now pending in the present application.

A. Pending Claims Contain Amendments Inherent to Previously Examined Claims and are Entitled to the Benefit of the Filing Date of the Parent Application.

Previously pending independent claim 1 which described a method of manufacturing a product of the present invention, has been amended to

recite inherent properties thereof. In particular, claim 1 now recites the limitation that the mixture obtained in the first step of the method is a "nitrate-free mixture" and that this mixture is processed to product "a nitrate-free product which is partially chelated". Claims 2-13 and 20-22 incorporate this limitation through their direct or indirect dependency from amended claim 1.

Amended claim 16 recites a composition "consisting essentially of a partially chelated mixture of a metal salt, citric acid and sodium citrate." Claims 17 and 18 incorporate this limitation through their dependence from amended claim 16.

Newly presented claim 23 recites "mixing a metal salt, citric acid and sodium citrate to obtain a nitrate-free mixture" and "processing the nitrate-free mixture in a drying environment to obtain a nitrate-free product which is partially chelated". Claims 24-30 incorporate these limitations through their dependence from claim 23.

Newly presented claim 31 recites a composition "comprising a nitrate-free, partially chelated mixture of a divalent metal salt, citric acid and sodium citrate" Claims 32-34 incorporate this limitation through their dependence from claim 31.

Each of these claims recite a product fully disclosed in Serial No. 08/755,236, and incorporate limitations which were inherent properties of the product. This conclusion is fully supported by the plain language of the specification of Serial No. 08/755,236, and by the Declaration Under 37 C.F.R. § 1.132 of Alan M. Robinett and Carl Schauble filed herewith

In conformance with the 1995 decision by the Court of Appeals for the Federal Circuit in Therma-Tru Corp. v. Peachtree Doors, Inc., 44 F.3d 988, 992-933, 33 U.S.P.Q.2d 1274 (Fed.Cir. 1995), each of these claims is entitled to the priority/filing date of the parent application. Accordingly, the claims now presented do not include any new matter.

B. All Pending Claims are Distinguishable over Kimbro.

Independent claims 1, 16, 23 and 31 (and dependent claims 2-13, 17-18, 20-22, 24-30 and 32-34) are clearly distinguishable over Kimbro, which mandates the inclusion of concentrated nitric acid in a mixture to produce a chelated product using a method in which the chelation process is driven to completion/stabilization. In contrast, claims 1, 23 and 31 recite the creation of a "nitrate-free" mixture and/or product. Claim 16 relates to a composition "consisting essentially of" a partially chelated mixture containing a metal salt, citric acid and sodium citrate.

As an initial matter, there is no suggestion in Kimbro to omit the concentrated nitric acid. *Prima facie* obviousness based on Kimbro is thereby initially overcome. M.P.E.P. § 2143; In re Fine, 837 F.2d 1071 (Fed. Cir. 1988); In re Jones, 958 F.2d 347 (Fed. Cir. 1992)

In addition, the proposed modification would render Kimbro unsatisfactory for its intended purpose, i.e., the Kimbro process would not be expected to proceed as described, and *prima facie* obviousness based on Kimbro is further overcome. In re Gordon, 733 F.2d 900 (Fed. Cir. 1984). M.P.E.P. § 2143.01

The case of *prima facie* obviousness is fully overcome because all claim limitations must be taught or suggested by the prior art. In re Royka, 490 F.2d 981 (C.C.P.A. 1974); In re Wilson, 424 F.2d 1382 (C.C.P.A. 1970); M.P.E.P. § 2143.03. Kimbro does not teach or suggest all of the limitations of claims 1-13, 16-18, and 20-34 and thus these claims are patentably distinguishable over Kimbro and the references of record.

C. Conclusion.

Allowance of the present case is respectfully requested. Should any issues remain, the Examiner is asked to telephone the undersigned.

Respectfully submitted,

March 20, 1998

  
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Carol W. Burton, Reg. No. 35,465  
HOLLAND & HART LLP  
Post Office Box 8749  
Denver, Colorado 80201-8749  
Telephone: (303) 295-8357  
Facsimile: (303) 295-8261

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Alan M. ROBINETT & Carl SCHAUBLE

Serial No.

Filed: March 19, 1998

For: METHOD OF MANUFACTURING  
CITRIC ACID CHELATES

Examiner:

Art Unit: 1103

DECLARATION UNDER 37 C.F.R. § 1.132  
OF ALAN M. ROBINETT & CARL SCHAUBLE

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

We, Alan M. ROBINETT and Carl SCHAUBLE, the inventors in the above-identified application, declare as follows:

1. We conceived in the United States the invention claimed in the above patent application, prior to November 22, 1996.


2. The partially-chelated products described in the above patent application and in its parent application, U.S. Patent Application Serial No. 08/755,236, were inherently free of nitrates.

3. The partially-chelated products described in the above patent application and in its parent application, U.S. Patent Application Serial No. 08/755,236 are identical.

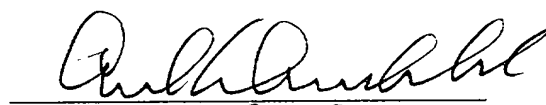
4. The terminology "nitrate-free" in the claims of the present application is included to distinguish over the prior art and does not change the invention that was disclosed in the parent application, U.S. Patent Application Serial No. 08/755,236.

5. The declarants further state that the above statements were made with the knowledge that willful false statements and the like are punishable by fine and/or imprisonment, or both, under Section 1001 of Title 18 of the U.S. Code, and that any such willful false statement may jeopardize the validity of this application or any patent resulting therefrom.

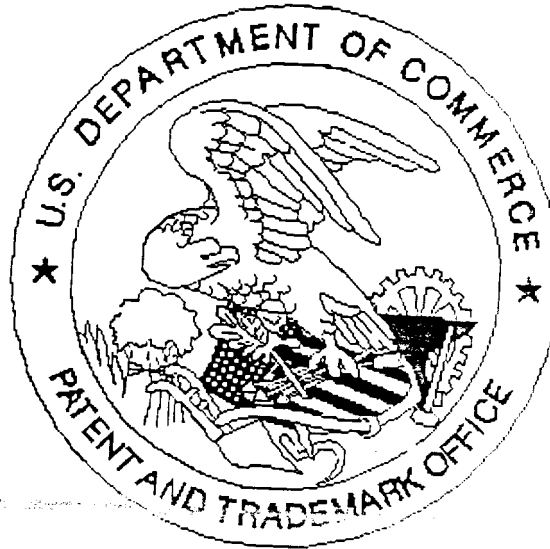
Alan M. Robinett:

  
Date: 3-18-98

Carl Schauble:

  
Date: 3-18-98

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